

PATENT SPECIFICATION

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(54) MULTILAYER PLASTICS CONTAINER

(71) We, THE STANDARD OIL COMPANY, a corporation organised under the laws of the State of Ohio, United States of America of Midland Building, Cleveland, Ohio 44115, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a multilayer plastics container and to a method of producing it. The plastics containers of this invention can be used in a wide variety of applications, particularly in the packaging of foods, beverages, drugs and cosmetics.

Considerable effort is being devoted to the recycling of plastics containers because of the concern for the maintenance of a clean environment and the conservation of energy. Many proposals have been made to recycle plastics containers and thus the amount of solid waste created by these materials as well as to decrease the consumption of fossil fuels, particularly petroleum oil, which are raw material sources for most plastics. Recycling of used plastics containers can involve (1) burning the used containers for their fuel value, (2) regrinding the used containers and use of the reground plastics in other applications such as fillers for asphalt or concrete or forming the regrind into articles such as a drain pipe, sewer pipe, and the like, and (3) careful screening and cleaning of the used containers, regrinding and reuse of the regrind along with some virgin plastics (freshly manufactured, not yet recycled) for containers for foods, beverages, drugs and cosmetics. Although (3) above would seem to be the most desirable option for recycling, it is doubtful that the screening and cleaning controls

would be adequate to insure that such reground plastics would ever meet the required standards for the virgin resin.

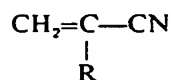
We have discovered that plastics containers useful for the packaging of foods, beverages, drugs and cosmetics as well as many other types of products sold to the consumer can be manufactured by employing a liner in the container of virgin (not previously used) resin and recycled plastics, that is the same material on the outside of the liner. Thus, the controlled-purity virgin resin always will be the only resin surface which contacts the food, beverage, drug, cosmetic or other product and the less pure, recycled plastics will be on the outside of the container to provide the physical strength and other properties required of the container. The virgin resin and recycled resin in the containers of the invention are identical material except for the aforementioned differences in source and consequently in purity. Thus, it is possible with our discovery to recycle plastics containers readily into new containers which are completely safe for use in the packaging of foods, beverages, drugs, cosmetics and other consumer products.

According to the invention therefore there is provided a container for the packaging of goods such as food, drugs and cosmetics composed of an inner goods contacting layer of virgin resin and an outer layer of recycled resin both layers being of the same nitrile barrier resin material as herein defined.

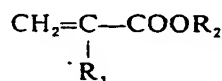
The invention further provides a process for the manufacture of such a container comprising forming a combination an inner parison and an outer parison from a plastics material, and blow-moulding a container from this combination, the inner parison being composed of virgin plastics and the outer parison being or recycled plastics,

both parisons being of the same nitrile barrier resin material as herein defined.

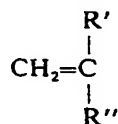
- 5 The nitrile barrier resins for use in the invention which have excellent gas barrier properties, chemical resistance and other very desirable properties are homopolymers and copolymers which result from the polymerization of 100 parts by weight of (A) at least 50% by weight of at least one nitrile having the structure



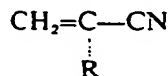
- 15 wherein R is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and (B) up to 50% by weight based on the combined weights of (A) and (B) of (1) an ester having the structure



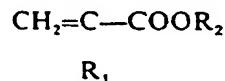
- 20 wherein R₁ is hydrogen, an alkyl group having from 1 to 4 carbons, or a halogen, and R₂ is an alkyl group having from 1 to 6 carbon atoms, (2) an alpha-olefin having the structure



- 25 wherein R' and R'' are alkyl groups having from 1 to 7 carbon atoms, (3) methyl vinyl ether, ethyl vinyl ether, a propyl vinyl ether, or a butyl vinyl ether, (4) vinyl acetate, (5) styrene, (6) indene or a mixture thereof, in the presence of from 0 to 150 parts by weight and preferably 0 to 40 parts by weight of (c) a rubbery polymer of a conjugated diene monomer which is butadiene and/or isoprene and optionally as comonomer styrene, a nitrile monomer having the structure



wherein R has the foregoing designation or a monomer having the structure



- 40 wherein R₁ and R₂ have the foregoing designations, said rubbery polymer containing from 50 to 100% by weight of polymerized conjugated diene and from 0 to 50% by weight of comonomer.

In the most preferred nitrile barrier resins used according to the invention, (A) is acrylonitrile, (B) is methylacrylate and (C) is a butadiene-acrylonitrile copolymer.

There are several techniques which may be used for producing the containers according to the invention including the use of dual injection moulding units to injection mold a container such as a bottle having a core of virgin plastics and an outside layer of recycled plastics. This container gives the appearance of having been made from a single material when finished with no problem involving refractive index differences. Another acceptable technique involves the insertion of a thermoformed tube of the virgin plastics on an injection mold core pin with subsequent injection of the recycled plastics prior to the blowing of the composite container. Two pipes of different diameters can be formed and tubes cut from these pipes can be meshed with one inside the other (tube of virgin plastics on the inside) and the composite blown to form a bottle or the like. Numerous other similar techniques can be employed for the production of the containers according to the invention.

The containers of this invention consist of a single plastics material and are composites of virgin plastics on the inside (product contact surface) and reground plastics on the outside which is not in contact with the product packaged therein. The innerlining of virgin resin can be colorless or tinted any color and the outer recycled layer can be clear or of the same or different color than the inner layer. For instance, in the case of a plastics beer bottle, the inner liner can be of a clear nitrile barrier resin and the outer layer can be recycled nitrile barrier resin color coded brown. The overall appearance of the bottle is brown.

In order that the invention may be more fully understood a preferred embodiment thereof will now be described with reference to the accompanying drawings in which:—

Figure 1 is a perspective view of a bottle partly in section.

Figure 2 is a side elevation view partly in section of the inner parison made from virgin resin.

Figure 3 is a side elevation view partly in section of the outer parison made from recycled resin.

Figure 4 is a side elevation view partly in section showing the composite parison.

Figure 5 is a view of the bottle taken along the line 5—5 in Figure 1.

Figure 6 is a view of the bottle taken along line 6—6 in Figures 1 and 5.

The bottle 1 is made from a combination of inner parison 2 and a parison of recycled resin 3 which is formed either independently

by injection molding or extrusion as shown in Figure 3, or by injection, or extrusion molding over the inner parison 2 as shown in Figure 4 to form a composite parison 4 which is then blow molded into the bottle 1 in a suitable bottle mold. The inner parison 2 can be made by thermoforming from virgin resin sheet, injection molding or extrusion of the virgin resin. It is preferred that the bottle be prepared in such a manner that the final thickness of the expanded parison 2 be at least one mil at its thinnest point in the bottle so that the material ultimately packaged in the bottle will be exposed only to virgin resin.

In the prior art it has been proposed in many cases to produce composite plastics structures employing at least two different types of plastics materials. The production of such composites presents problems of proper bonding, extrusion viscosities, and the like, which are not problems at all in the homogeneous composite structures provided by this invention.

The present invention provides a ready means for employing high levels of recycled plastics without influencing the effectiveness of the container to produce containers which can be used safely in packaging foods, beverages, drugs and cosmetics. In the commercial application of the invention, a plant manufacturing beer bottles of nitrile barrier resins, for instance, could run varying levels of virgin material to compensate for variations in the availability of the recycled material.

Because the containers of this invention have excellent solvent resistance, water resistance, and low permeability to gases and vapors, they are useful in the packaging industry in the form of bottles, envelopes, boxes, and the like, for containing solids and liquids.

In the following example, which will further illustrate this invention, the amounts of the various ingredients are given in parts by weight unless otherwise specified.

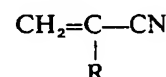
Example

A bottle was prepared from Barex (Registered Trade Mark) 210 resin, a nitrile rubber-modified acrylonitrile-methyl acrylate copolymer, more fully described in U.S. Patent No. 3,426,102. An extruded sheet of the virgin resin having a thickness of from 20 to 30 mils was vacuum thermoformed over a mandrel to give an inner parison of the type shown in Figure 2 of the accompanying drawings. The inner parison was placed over the core pin of an injection blow molding machine and an outer parison of recycled Barex 210 resin was injection molded over the inner parison to give a composite parison of the type shown in Figure 4. The composite was then

brought to a temperature of about 220 to 250°F and placed in a blow mold station, and a biaxially oriented bottle of the type shown in Figure 1 of the accompanying drawings was blown. The entire interior of the bottle thus formed was made up of virgin resin and was suitable for contacting foods and beverages of all types.

WHAT WE CLAIM IS:—

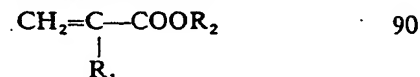
1. A container for the packaging of goods such as food, drugs and cosmetics composed of an inner goods contacting layer of virgin resin and an outer layer of recycled resin both layers being of a resin material which results from the polymerization of 100 parts by weight of (A) at least 50% by weight of at least one nitrile having the structure



wherein R is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and

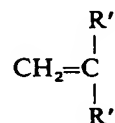
(B) up to 50% by weight based on the combined weight of (A) and (B) of

(1) an ester having the structure



wherein R₁ is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and R₂ is an alkyl group having from 1 to 6 carbon atoms,

(2) an alpha-olefin having the structure



wherein R' and R'' are alkyl groups having from 1 to 7 carbon atoms,

(3) methyl vinyl ether, ethyl vinyl ether, a propyl vinyl ether or a butyl vinyl ether,

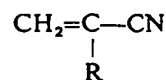
(4) vinyl acetate,

(5) styrene,

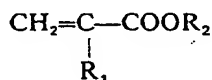
(6) indene, or a mixture thereof;

in the presence of from 0 to 150 parts by weight of

(C) a rubbery polymer of a conjugated diene monomer which is butadiene and/or isoprene and optionally as comonomer styrene, a nitrile monomer having the structure



wherein R has the foregoing designation or a monomer having the structure



wherein R₁ and R₂ have the foregoing designations, said rubbery polymer containing from 50 to 100% by weight of polymerized conjugated diene and from 0 to 50% by weight of comonomer.

2. A container as claimed in claim 1 in which (A) is acrylonitrile.

3. A container as claimed in claim 2 in which (B) is methyl acrylate.

4. A container as claimed in claim 3 in which (C) is a butadiene-acrylonitrile copolymer.

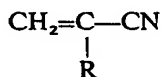
5. A container as claimed in any of claims 1 to 4 in the form of a bottle.

6. A container as claimed in any of claims 1 to 5 in which the contact layer is at least one mil thick.

7. A container as claimed in claim 6 substantially as herein described with reference to the Example and the accompanying drawings.

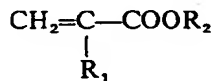
8. A process comprising forming in combination an inner parison and an outer parison from a plastics, and blow molding a container from said combination, said inner parison being composed of virgin plastics and said outer parison being composed of recycled plastics, both parisons being of the same plastics material, which is one resulting from the polymerization of 100 parts by weight of

(A) at least 50% by weight of at least one nitrile having the structure



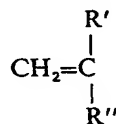
wherein R is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen, and

(B) up to 50% by weight based on the combined weights of (A) and (B) of (1) an ester having the structure



wherein R₁ is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a

halogen, and R₂ is an alkyl group having from 1 to 6 carbon atoms,
(2) an alpha-olefin having the structure



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wherein R' and R'' are alkyl groups having from 1 to 7 carbon atoms,

(3) methyl vinyl ether, ethyl vinyl ether, a propyl vinyl ether or a butyl vinyl ether,

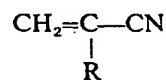
(4) vinyl acetate,

(5) styrene,

(6) indene, or a mixture thereof;

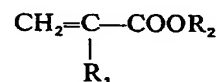
in the presence of from 0 to 150 parts by weight of

(C) a rubbery polymer of a conjugated diene monomer which is butadiene and/or isoprene and optionally as comonomer styrene, a nitrile monomer having the structure



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wherein R has the foregoing designation, and a monomer having the structure



wherein R₁ and R₂ have the foregoing designations, said rubbery polymer containing from 50 to 100% by weight of polymerized conjugated diene and from 0 to 50% by weight of comonomer.

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9. A process as claimed in claim 8 in which (A) is acrylonitrile.

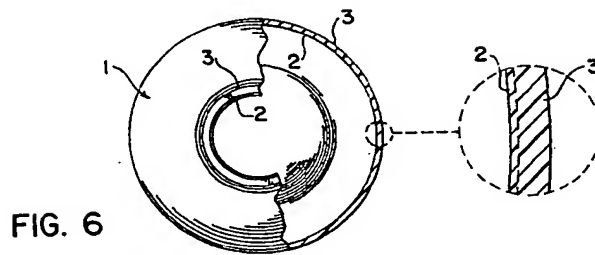
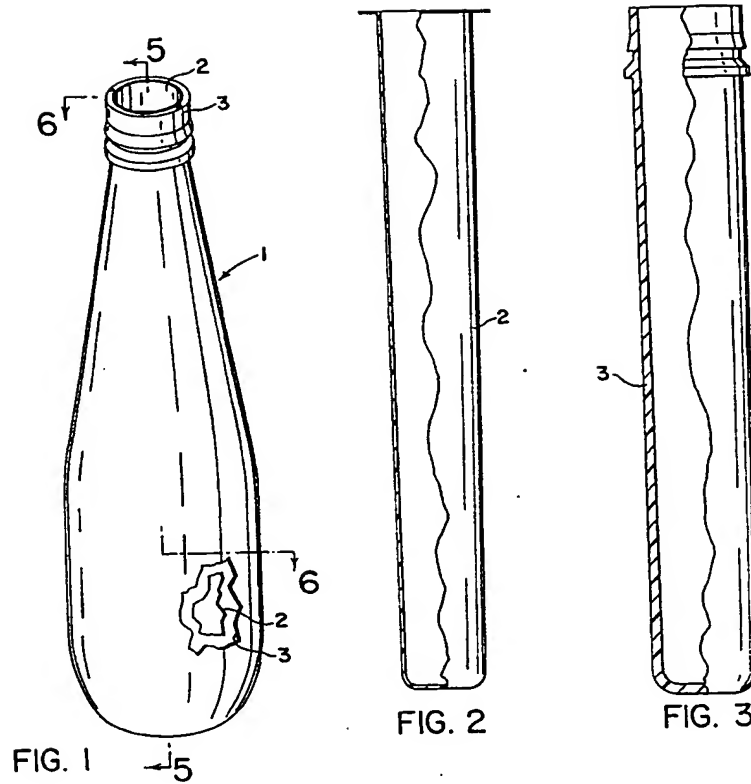
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10. A process as claimed in claim 8 substantially as herein described with reference to the Example and the accompanying drawings.

11. A container when made by a process as claimed in any of claims 8 to 10.

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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale*

Sheet 2

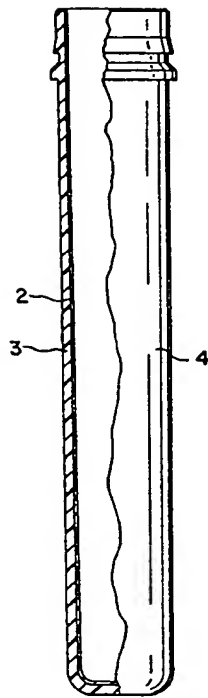


FIG. 4

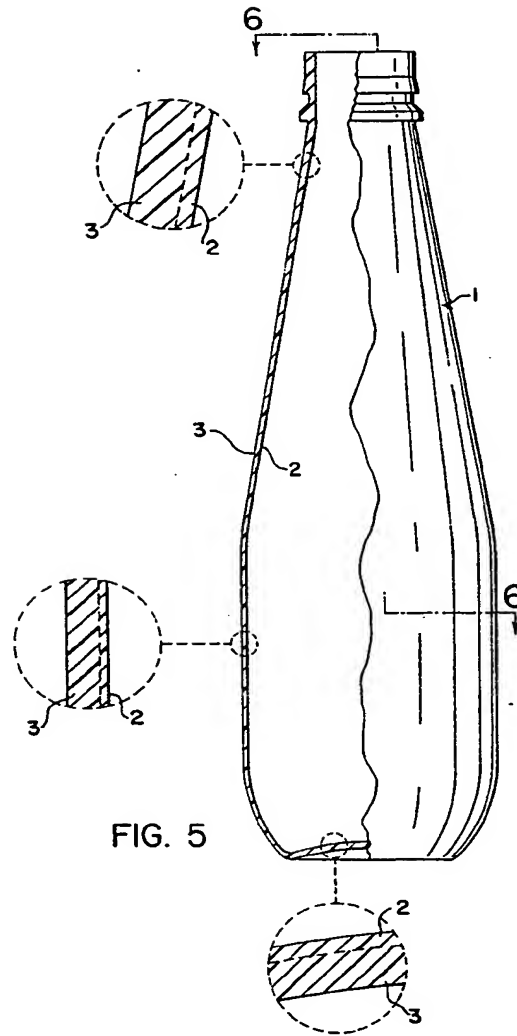


FIG. 5

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